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WITNESS my hand this
Fourteenth day of January 2004

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PROVISIONAL SPECIFICATION

Applicant(s):

    INTEC LTD

Invention Title:

    REMOVING CONTAMINANTS FROM SULFIDIC MATERIALS

The invention is described in the following statement:

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REMOVING CONTAMINANTS FROM SULFIDIC MATERIALS

Field of the Invention

5   The present invention relates to a method for removing a contaminant from a sulfidic material. The present invention also relates to the recovery of product (eg. economically valuable metals) from a sulfidic material.

The present invention has been primarily developed
10   for removing environmentally hazardous contaminants, such as arsenic, antimony and bismuth, from sulfidic materials, especially pyritic ores. In this regard, the invention can be applied to contaminated sulfidic materials having a high carbon content (a so-called "double-refractory
15   material") or no or low carbon content (a so-called "single-refractory material") and will be described with reference to such applications. In addition, the invention allows for the recovery of precious metals such as gold, silver etc. which may be present in the
20   contaminated sulfidic material. However, it should be appreciated that the invention has broad application to a wide variety of sulfidic ores, not only for metal recovery, but also in the processing of waste materials and residues for subsequent disposal.
25

Background to the Invention

Across the world there are significant deposits and quantities of sulfidic materials including economically desirable metals to recover, especially precious metals
30   such as gold and silver. For example, there are significant deposits and stockpiles of pyritic ores including gold and/or silver and other precious metals, however a number of these deposits are contaminated with difficult to process contaminants such as arsenic,
35   antimony, bismuth or other heavy metals. Ore treatment may also be complicated when high levels of carbon are present, as carbon associates with and has a high affinity

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for precious metals such as gold.

Where a sulfidic material includes a contaminant such as arsenic, the use of conventional smelting or roasting techniques to treat the material for metal recovery result

5 in the formation of eg. arsenic trioxide which is difficult to collect and highly toxic so should not be released to the environment. Also, high levels of sulfur in a smelting or roasting feed produces high levels of sulfur dioxide and other SO_x gases in the exhaust.

10   US6461577 discloses a process for treating sulfidic materials containing arsenic where the sulfidic material is subjected to a two-stage bio-leaching process to solubilise the arsenic. The configuration of the leaching process is complex, as is the use of bio-leaching

15 bacteria. In addition, bio-leaching is notoriously slow.

It would be advantageous if an alternative hydrometallurgical process could be provided for treating contaminated sulfidic ores and concentrates, with the attendant advantages of hydrometallurgical processing

20 (including process simplicity, absence of emissions, lower energy requirements etc.).

Summary of the Invention

In a first aspect the present invention provides a

25 method of removing a contaminant from a sulfidic material comprising the steps of:

•mixing the material in an aqueous solution wherein a multi-valent species of a relatively high oxidation state oxidises the contaminant to render it soluble in the

30 solution, produces a contaminant refined material, and is reduced to a relatively lower oxidation state; and

•removing the contaminant from the solution whilst regenerating the multi-valent species to its relatively high oxidation state.

35   Advantageously, by removing the contaminant whilst regenerating the multi-valent species, the method can be operated in a closed loop or recycle mode with attendant

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economic benefits (eg. simplicity, low energy consumption, preservation of mass balance etc.).

In a second aspect the present invention provides a method of removing a contaminant from a sulfidic material
5 comprising the steps of:
•mixing the material in an aqueous solution having an oxidation potential controlled to oxidise substantially only the contaminant to render it soluble in the solution, thereby producing a contaminant refined material; and
10 •separating the solution from the contaminant refined material.

Advantageously, by controlling the oxidation potential the method enables the contaminant to be maintained in a soluble form, thus facilitating subsequent
15 removal (eg. in a separate precipitation step). For example, where the material is an arsenopyrite and the contaminant is arsenic, the oxidation potential can be controlled such that the arsenic is oxidised to its +3 oxidation state rather than its relatively less soluble +5
20 state. Once the arsenic has been solubilised and separated the remaining pyrite component can then be oxidised more vigorously in a subsequent stage.

The terminology "contaminant refined material" includes a material in which contaminant has not been
25 completely removed therefrom, but which has sufficiently low contaminant levels such that it can be acceptably further processed (eg. in roasters and smelters) or meets acceptable environmental standards for disposal etc.

The inventors have also observed that the method of
30 the first and second aspects can be applied to otherwise difficult to treat ores and concentrates including arsenopyrites, especially double-refractory ores having a high carbon content.

Preferably the contaminant is removed from the
35 solution by precipitation in a separate precipitation stage by introducing an oxidant into the solution.

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Preferably the oxidant simultaneously causes the multi-valent species to be oxidised to its relatively high oxidation state. Preferably after precipitating and removing the contaminant and regenerating the multi-valent

5 species to its higher oxidation state, the solution is recycled to the leaching stage.

Preferably in the precipitation stage the solution pH is maintained at around pH 1.5-3. Preferably the solution pH is maintained by regulating the supply to the solution

10 of the oxidant and/or an alkali agent. When addition of an alkali agent is required an alkali salt such as calcium carbonate, calcium oxide, sodium carbonate, sodium bicarbonate etc. is typically added.

Typically in the precipitation stage the oxidant

15 causes the contaminant to precipitate by oxidising it to a relatively less soluble form (eg. oxidising arsenic from its +3 to +5 oxidation state), and at the same time oxidises the multi-valent species. Typically the oxidant is air, oxygen, chlorine gas, hydrogen peroxide etc. In

20 pyritic ores the contaminant typically precipitates as an iron/contaminant-oxidate form (eg ferric arsenate when the contaminant is arsenic).

Preferably after contaminant precipitation, solution Eh and pH are restored to levels required for contaminant

25 leaching, to enable solution recycle to the leaching stage. This can be achieved by eg. regulating the addition of oxidant after contaminant precipitation.

Preferably the contaminant is oxidised in a single or multi stage leaching process.

30 Preferably the leaching process comprises a first leaching stage in which the oxidation potential is controlled to oxidise substantially only the contaminant to render it soluble in the solution, and a second leaching stage in which the oxidation potential is

35 increased to oxidise sulfide in the contaminant refined material. In this regard, preferably a bulk of contaminant is oxidised and solubilised in the first leaching stage

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with residual contaminant being oxidised in the second leaching stage.

Each leaching stage may be operated co- or counter-currently and in this regard, each stage may comprise one
5 or more vessels.

Preferably the contaminant refined material that is separated from the solution after the first leaching stage is fed to the second leaching stage.

Preferably the solution is separated from the
10 contaminant refined material after each leaching stage for removal of contaminant therefrom, typically by precipitation in the precipitation stage.

Preferably when the sulfidic material is a pyritic material (and noting that "pyritic" includes arsenopyrite
15 and other contaminated pyrites), in the first leaching stage the contaminant is oxidised in a highly acidic aqueous solution of pH typically less than 1, at a solution Eh sufficient to oxidise the contaminant into solution but not substantially leach pyrite, preferably at
20 an Eh of around 0.5 volts, and preferably at a temperature of about 105°C.

Preferably in the second leaching stage the pyritic material is also oxidised in a highly acidic aqueous solution of pH typically less than 1, but at a higher
25 solution Eh sufficient to leach pyrite, preferably at an Eh of around 0.6 volts, and at a temperature of about 105°C. To achieve the higher solution Eh in the second leaching stage, typically an oxidant such as oxygen, air, chlorine gas, hydrogen peroxide etc. is added to the
30 solution and, as necessary, an acid such as sulfuric acid may be added.

In this regard, in the second leaching stage, to maintain a low solution pH and thereby solubilise arsenic which is now present in its +5 oxidation state, the
35 addition thereto of an acid may also be required, such as sulfuric acid, hydrochloric acid or any other acid which does not interfere with the process chemistry. However,

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the addition of an acid may not be required (eg. where sulfur present in the ore or concentrate is oxidised and thereby generates sufficient sulfuric acid in the solution)

5   Most preferably the solution employed throughout the leaching and precipitation stages (which is typically recycled in the overall process) is a dissolved metal chloride solution, typically having a chloride concentration of approximately 7 moles per litre. The

10   method is preferably operated such that the metal in the dissolved metal chloride solution functions as the multi-valent species (however a multi-valent species may be separately added to the leaching process solution). In this regard, typically the metal in the metal chloride

15   solution is copper, but may also be iron etc. The multi-valent species effectively acts as an electron transfer agent. For example, in the solution recycled to the leaching stage the metal is in its relatively high oxidation state (eg. Cu(II) or Fe(III)) and after

20   oxidation is in its relatively lower oxidation state (eg. Cu(I) or Fe (II)). However, other multi-valent species may be employed including possibly cobalt, manganese and vanadium.

        As stated above, typically the sulfidic material is
25   a pyritic ore or concentrate, and typically the contaminant is arsenic, antimony, bismuth, mercury, cadmium, which occur naturally in many as-mined sulfidic materials.

        A number of pyritic ore deposits around the world
30   have a high carbon content and, when a high level of carbon is present in the sulfidic material (eg. 2-20 wt% carbon), a surfactant such as a blinding agent can advantageously be added to the solution during the contaminant oxidation (leaching) step to prevent any

35   dissolved metals (especially precious metals such as gold) from adsorbing onto carbon in the material. The blinding agent is typically one or more organic solvents including

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kerosene, phenol ethers, etc. The use of a blinding agent
may obviate the need for roasting to separate the precious
metal from the carbon.

Preferably, after precipitating and removing the
5   contaminant and regenerating the multi-valent species to
its relatively high oxidation state, the solution is
recycled to the leaching stage. Recycling the solution to
the leaching stage is desirable for overall process
economics and is advantageous because the multi-valent
10   species is regenerated to its original (pre-leaching)
oxidation state, and thus is ready to participate in
further oxidation and leaching.

In a typical application of the present invention,
the sulfidic material includes, in addition to the
15   contaminant, a metal to be recovered. In this regard, the
method preferably further comprises a metal recovery stage
to recover metal from the separated contaminant refined
material.

In the case of a double-refractory ore, preferably
20   the metal recovery stage is provided as a separate,
subsequent stage, to recover metal present in contaminant
refined material solids from the leaching process. In this
regard, where the double-refractory ore includes carbon,
preferably the metal to be recovered (eg. gold) passes
25   with the carbon through the leaching process.

In the case of a double-refractory ore, an additional
in-line metal recovery stage may be provided subsequent to
contaminant precipitation (ie. intermediate to contaminant
precipitation and recycle to the oxidation stage) or prior
30   to contaminant precipitation (ie. intermediate to
contaminant oxidation and precipitation) to remove any
metal that is solubilised or present in the solution
separated from the leaching stage. Use of the terminology
"in-line" refers to a stage located on the solution
35   circuit (ie. as a result of solution recycle from
contaminant removal (precipitation) to leaching).

Also, in the case of a double refractory ore, because the contaminant has been substantially removed from the sulfidic material during leaching, the metal recovery stage may comprise a conventional roasting or smelting process. Optionally chlorine or cyanide leaching may be employed after roasting to recover any remaining metal in the roasted solids material (for example, where the metal is a precious metal such as gold).

In the case of a single refractory ore (eg. where carbon is not present at all or in any significant quantity, or where the metal is not associated with carbon) preferably the metal recovery stage is provided in-line and subsequent to contaminant precipitation, but may also be provided prior to contaminant precipitation. In this regard, preferably metal recovery involves adsorption of the metal in solution onto carbon in a carbon column, typically activated carbon. Alternatively, other metal recovery processes may be employed including ion exchange, solvent extraction, etc.

Typically the metal to be recovered is a precious metal such as gold, silver, platinum or other platinum group metals, the recovery of which metal typically justifies the process economics. However, other economically significant metals may alternatively or additionally be recovered including copper, nickel, zinc, lead etc. In addition, in certain applications the contaminant may itself be desirable or necessary to recover. For example, the contaminant may be economically valuable or environmentally harmful, prompting its recovery from the contaminant precipitate (eg. this may be the case for a contaminant such as antimony, bismuth, cadmium etc.). When the contaminant constitutes the "metal" to be recovered, a recovery stage can additionally or alternatively be provided after contaminant precipitation.

Preferably, prior to metal recovery, the method further comprises a number of material separation stages

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to separate the contaminant refined material from the
solution. In this regard, preferably after the first
leaching stage the solution is subjected to a thickening
stage to thicken and separate contaminant refined material
5 from the solution. Preferably after the second leaching
stage the contaminant refined material is filtered from
the solution, however other separation methodologies may
be employed such as solid/liquid settling, solution
evaporation, centrifugation etc.

10   Thus, typically the separated solution after each of
the first and second leaching stages is passed to
contaminant recovery, whereas the separated refined
material is typically passed to metal recovery (double-
refractory) or disposal (single-refractory).

15   After the contaminant precipitation stage, preferably
the method further comprises a contaminant separation
stage to remove the contaminant from solution prior to in-
line metal recovery, and prior to recycling the solution
to the leaching stage. In this regard, a solid/liquid
20 separation stage is preferably employed after contaminant
precipitation. Typically this solid/liquid separation
stage is facilitated by filtration, but again other
separation methodologies may be employed.

          In a third aspect, the present invention provides a
25 method of removing arsenic from a gold-bearing pyritic
material comprising the steps of:
•leaching the material in a leaching stage wherein the
material is mixed with an acidic aqueous metal chloride
solution in which the metal has a relatively high
30 oxidation state, such that the metal oxidises the arsenic
to render it soluble in the solution, produces a pyritic
material refined of arsenic, and is reduced to a
relatively lower oxidation state;
•precipitating and separating the arsenic from the solution
35 in a precipitation stage whilst simultaneously
regenerating the metal to its relatively high oxidation
state; and

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•returning the solution to the leaching stage with the metal in its relatively high oxidation state.

In a fourth aspect, the present invention provides a method of removing arsenic from a gold-bearing pyritic
5   material comprising the steps of:
•leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride solution having an oxidation potential controlled to oxidise substantially only the arsenic to render it
10   soluble in the solution, thereby producing a pyritic material refined of arsenic; and
separating the solution from the refined pyritic material.

In a fifth aspect the present invention provides a method of treating a relatively high carbon content
15   sulfidic material contaminated with a contaminant to allow recovery of a precious metal present with the material, comprising the steps of:
•leaching the material in an aqueous solution wherein the contaminant and metal are solubilised in the solution,
20   whilst masking the carbon in the material to prevent precious metal adsorption thereon; and
•recovering the precious metal from the solution.

When the term "relatively high carbon content" is used herein it refers to a carbon content in the sulfidic
25   material that is typically higher than about 2 wt%.

Preferably, the carbon is masked by adding a surfactant such as a blinding agent (as defined above) to the solution during leaching.

Typically the method of the third, fourth and fifth
30   aspects is otherwise as conducted in the first and second aspects of the invention.

Brief Description of the Drawings

Notwithstanding any other forms which may fall within
35   the scope of the present invention, preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

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Figure 1 schematically depicts a generalised process flow diagram illustrating removal of a contaminant from a sulfidic material, with associated recovery of precious metal from the sulfidic material;

5   Figure 2 schematically depicts a process flow diagram for a preferred method of removing a contaminant from a single-refractory sulfidic material and recovery of precious metal from the sulfidic material;

Figure 3 schematically depicts a process flow diagram
10   for a preferred method of removing a contaminant from a double-refractory sulfidic material and recovery of precious metal from the sulfidic material; and

Figure 4 is a graph plotting various first stage (arsenic) leaching solution parameters against time
15   (duration of reaction); and

Figure 5 is a graph plotting various second stage (pyrite) leaching solution parameters against time (duration of reaction).

20   **Modes for Carrying out the Invention**

Prior to describing preferred methods of the invention by way of detail and example, a preferred method according to the present invention will first be described in overview with reference to Figure 1.

25   Referring to Figure 1, a precious metal concentrate 10 for feeding to the process is prepared by mining, milling and then flotation of a sulfidic ore. The concentrate may be a gold-containing arsenopyrite of high carbon content (eg. 2 to 20 wt% carbon) or may have low or
30   no carbon content (eg less than 2 wt%). The concentrate is ground in a ball mill 12 and is then fed to a contaminant oxidation stage in the form of arsenic leaching process 14.

The preferred arsenic leaching process is described
35   below in greater detail with reference to Figures 2 & 3 and Examples 8 & 9. Leaching may be conducted in a single stage (eg. having one or more processing units, vessels or

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tanks), but typically is conducted in a multi (two) stage
process. Each stage can have one or more processing units,
vessels or tanks operated in a co-current or
countercurrent leaching configuration, and employing over
5   and underflows (as is known).

In either case, in the leaching process 14 a highly
acidic environment is maintained (preferably less than pH
1, as leaching of arsenic from arsenopyrite is favoured by
low solution pH). The acid environment can be achieved
10   solely by the oxidation of the sulfidic material (eg.
where sulfur in the material is oxidised in solution to
sulfate) and/or a non-contaminating acid may be added
(such as sulfuric or hydrochloric acid).

Also, in accordance with the invention the leaching
15   solution Eh is typically maintained at greater than 0.4
volts (see Figure 4) to solubilise the contaminant. As
described below with reference to Figures 2 & 3 and the
Examples, preferably the leaching process has two stages.
In a first leaching stage the solution Eh is carefully
20   controlled to promote oxidation and solubilisation of
arsenic in its +3 oxidation state rather than its
relatively less soluble +5 state, whilst not substantially
oxidising pyrite in the arsenopyritic material. In a
second leaching stage an oxidant (such as oxygen, air,
25   chlorine, hydrogen peroxide etc) is added to raise the
solution oxidation potential and thereby oxidise the
pyrite (which at the same time oxidises any remaining
arsenic to its +5 oxidation state). To maintain As(V) in
solution in the second leaching stage an acid (such as
30   sulfuric acid) may need to be added to lower the solution
pH sufficient to solubilise the arsenic.

The process solution is typically an aqueous cupric
chloride solution, preferably having a chloride
concentration of 7 moles/litre. In the leaching stage the
35   cupric ion oxidises the sulfidic material to leach the
arsenic etc. into solution. At the same time, the cupric
ion is reduced to cuprous ion. Thus, in the process, the

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copper acts as an electron transfer agent. Other agents can perform this function, including iron, cobalt, manganese, vanadium, etc.

Where the sulfidic material has a high carbon content
5   (eg. greater than 2 wt%) a masking surfactant may be added to the solution at stage 14 to prevent adsorption onto carbon of any precious metal leached into the solution. The surfactant is typically an organic blinding agent such as kerosene, a phenol ether etc.

10   The present inventors have surprisingly found that at an acid pH less than 1, and at a controlled Eh (oxidising potential) in the range of from 0.4 to 1.25 volts, in fact optimally at around a relatively modest oxidising potential of 0.5 volts, arsenic can be oxidised and
15 leached into solution in its relatively soluble +3 oxidation state, and without oxidising pyritic sulfide to sulfate.

In a first leaching stage the arsenopyrite concentrate is leached for a predetermined period of time
20 (as described below in the Examples) until a predetermined amount of arsenic has been leached out of the arsenopyrite material (typically around 85% of total in the first leaching stage and an additional 10% of total in a second leaching stage). In any case, the amount leached is
25 typically determined by acceptable residual levels in the leached arsenopyrite material, assuming that it is to be separated and subsequently processed by conventional smelting or roasting techniques, or disposed of (as described below). The term "refined arsenopyrite" or
30 "refined sulfidic material" is thus to be interpreted in this regard.

In accordance with the invention, the solution pH and solution Eh are regulated such that arsenic and the multi-valent species Cu(II) (which oxidises and leaches the
35 arsenic from the material) remain in solution and do not precipitate therefrom in the first leaching stage. In addition, the process operating conditions are controlled

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such that the arsenic is maintained in solution during solid/liquid separation (which separates the refined arsenopyrite from the solution) until the solution is fed to an arsenic precipitation stage.

5 Thus, after leaching the solution (leachate) is separated from the refined arsenopyrite. In Figure 1 this is depicted schematically as a thickening stage 16. In Figures 2&3 this thickening stage is employed after a first leaching stage (described below). In thickening

10 stage 16 the refined arsenopyrite solids are flocculated (ie. by adding thereto a flocculating agent), with the solids dropping out as an underflow stream 18 and the arsenic pregnant supernatant solution passing out of the thickening stage as an overflow stream 20. In Figure 1

15 the underflow or slurry 18 is then passed to a solid-liquid separation stage 22, where typically the solids are filtered from the solution using known filtering apparatus.

The resulting liquid filtrate 24 is returned to

20 overflow stream 20, whereas the filtered solids (ie. refined arsenopyrite) 26 are passed to a conventional roasting stage 28 and conventional cyanide leaching stage 30 for recovery of gold product 32.

Depending on the degree of leaching of precious metal

25 in arsenic leaching stage 14, some gold may pass with combined liquid stream 34, being the combination of streams 20 and 24, and be recovered in an in-line precious metal recovery stage 36. The recovery stage may comprise one or more columns filled with activated carbon through

30 which the solution is passed upwardly, such as in a fluidised bed arrangement. Dissolved gold (or other precious metal) in the solution adsorbs onto the carbon, whilst the dissolved arsenic in solution passes through the column as an overflow liquid stream 38. The activated

35 carbon bearing gold is then removed periodically and passed as a gold product stream 40 (together with gold

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product stream 32) to a gold recovery process (eg. by burning or eluting the carbon product).

From metal recovery stage 36, the solution 38 (including dissolved arsenic) is passed to a contaminant precipitation stage in the form of arsenic precipitation stage 42. Stage 42 is typically operated at pH 1.5-3. In stage 42 an oxidant is introduced (eg. sparged) into the solution (eg. as air, oxygen, chlorine etc.) to raise the solution oxidising potential (Eh), causing the dissolved arsenic to form a precipitate (typically arsenic forms an insoluble ferric arsenate precipitate (ie. $FeAsO_4$ or scorodite) in this pH range). Where the contaminant includes eg. antimony, the contaminant can assume the insoluble form ferric antimonate. However, as the contaminant precipitate forms, an acid is typically generated. Thus, addition of an alkali may be required to consume acid and maintain optimum solution pH and Eh. Typically the alkali is an alkali salt such as calcium carbonate, calcium oxide etc.

Thus, in further accordance with the invention the addition of oxidant and alkali is regulated to maintain optimum pH and Eh levels in the contaminant precipitation stage until all contaminant is precipitated. Thereafter, the solution pH and Eh levels are preferably restored to those of the leaching stage 14, so that after contaminant precipitation the solution can be recycled to that stage.

Also, in accordance with the invention, in the precipitation stage the oxidant causes the cuprous copper to be oxidised to cupric copper, thus regenerating this species and allowing for its recycle and reuse. In other words, advantageously, the regulation of solution Eh and pH promotes the re-oxidation of the multi-valent species whilst maintaining it in solution at all times so that, in the overall process, copper alternates between its +1 oxidation state and +2 oxidation state). In other words, the multi-valent species functions in the process as an electron transfer agent and, when the solution is recycled

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to the arsenic leach stage, the multi-valent species is
ready to participate in further contaminant oxidation
(leaching). Regeneration of the multi-valent species
enhances the process economics, simplifies the process and
5   allows the process mass balance to be completed.

        After arsenic precipitation, the solution includes
entrained arsenic precipitate. The solution is separated
from the arsenic precipitate in a solid/liquid separation
stage. In Figure 1 this is depicted schematically as a
10   further thickening stage 44, to produce a solids (arsenic
precipitate) underflow 46, which is then passed to a
solid-liquid separation stage 48. A supernatant liquid
overflow stream 50 is passed out of the top of the
thickening stage 44.   In the solid liquid separation stage
15   48, typically the arsenic precipitate is filtered out
using a filtration apparatus, producing a waste arsenic
product 52.   The liquid filtrate is returned to the
overflow stream 50 as liquid flow 54.   The combined liquid
stream 56 is then passed to a further precious metal
20   recovery stage 58, for example, an activated carbon column
etc to recover any metal not recovered at stage 36.
Alternatively stage 58 can be used instead of stage 36.
The resultant precious metal and activated carbon stream
60 is combined with the other precious metal recovery
25   streams 40 and 32, whilst a solution overflow 62 is
recycled to the arsenic leaching stage 14 to close the
process recovery loop.

        Optionally, depending on whether or not there is
contaminant build up in the overall process, a proportion
30   of the recycle stream 62 may be recycled to a bleed
circuit 64 to separate out any contaminant not recovered
in the arsenic precipitation stage and optionally any
other contaminants such as Mn, Cd, Ni, Co etc.

        Now that the process has been described in overview,
35   preferred process flowpaths will be described with
reference to Figures 2 & 3.

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Figure 2 shows a process flowsheet for the treatment
of a single-refractory sulfidic material. In Figure 2,
like reference numerals are used to denote similar or like
process stages to that of Figure 1. In a similar manner to

5   Figure 1, a gold-bearing arsenopyritic concentrate of low
or no carbon content (i.e. single-refractory) is prepared
and ground 10,12. The ground concentrate is then fed to a
preferred leaching process in accordance with the present
invention. The preferred leaching process has two stages,

10   namely, a first arsenopyritic (FeAsS) leaching stage 70
and a second pyritic (FeS$_2$) leaching stage 72.

The arsenopyritic concentrate is thus fed to first
leaching stage 70 wherein the leaching conditions are
controlled such that substantially only the arsenic in the

15   concentrate is oxidised and leached into solution and not
the pyritic component of the concentrate. In this regard,
the leaching conditions in first leaching stage 70 are
controlled such that the oxidation potential Eh is around
0.5 volts, the solution pH is less than 1, and the

20   solution temperature is maintained at about 105°C (although
can be operated in a range between 80°C and 105°C). These
conditions were observed by the inventors to be optimal
for the leaching of arsenic into solution in its soluble
+3 oxidation state from an arsenopyritic concentrate. As

25   discussed below in Example 8, after about 6 hours of
leaching, approximately 85% of the total arsenic in the
arsenopyritic concentrate was leached into solution in its
+3 oxidation state.

Once a predetermined amount of arsenic has been

30   leached into solution, the solution and concentrate (i.e.
arsenic refined arsenopyrite) is passed to a thickening
stage 16 in a similar manner to the process described in
Figure 1. Refined arsenopyrite solids are flocculated and
drop out as underflow stream 18, whereas the arsenic

35   pregnant supernatant solution passes out of the thickener
as overflow stream 20 to arsenic precipitation stage 42.

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In accordance with the present invention the refined
arsenopyrite solid stream 18 is now passed to the second
leaching stage 72 for leaching of pyrite. The oxidising
conditions in the second leaching stage are more severe
5   than the first leaching stage. In this regard an oxidant
such as oxygen is sparged into the solution so that the
oxidation potential Eh is increased to approximately 0.6
volts. In addition, the temperature of the solution in the
second leaching stage is maintained at around 105°C. The pH
10 of the solution in the second leaching stage is maintained
at less than pH 1.

Because acid is consumed in the second stage leaching
process (ie. as $Cu(II)$ and $Fe(III)$ are reduced to $Cu(I)$
and $Fe(II)$ respectively) it may be necessary to
15 periodically or continuously supply acid to the solution,
such as sulphuric acid, hydrochloric acid or another acid
that does not interfere with the process chemistry.
However, the top-up of acid depends on whether sufficient
sulfuric acid is produced by the leaching of pyrite.
20 Maintaining low pH in the second leaching stage also helps
solubilise $As(V)$.

In any case, in the second leaching stage sulfide is
oxidised through to sulfate, iron is leached into solution
as $Fe(III)$ and a proportion of any remaining arsenic in
25 the arsenopyritic ore is also leached into solution. The
inventors have observed that a further 10% of the total
arsenic can be leached into solution, such that final
residual arsenic from the leaching process is at 5% of
total in the concentrate feed. This equates with arsenic
30 levels that are sufficiently low for the residues from the
process to be safely disposed of.

The leachate from second leaching stage 72 is passed
as a stream 74 to a solid-liquid separation stage 22,
similar to Figure 1, where the residual solids are
35 filtered from the solution and a liquid filtrate stream 24
is returned to and combined with overflow stream 20 for
passing to arsenic precipitation stage 42. Solid residues

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filtered out at stage 22 are then passed to tails as
stream 76, either as filtered solids or as a slurry. In
this regard, water may be added at stage 22 to maintain
water levels in the process and/or to top up water that is
5   lost with the process residue.

In further accordance with the present invention,
gold or other precious metal is often present in the
single refractory arsenopyritic material and pyritic
material. Because the gold or precious metal is not
10   associated to any significant extent with carbon in the
single refractory material it may thus be leached into
solution in both the first and second leaching stages and
can therefore be recovered in the process circuit.
However, prior to gold or other precious metal recovery,
15   arsenic (or like contaminant) is removed from the process
solution in arsenic precipitation stage 42.

In this regard, and as described above, the pH of the
solution is adjusted to approximately 2 to 3 (e.g. by the
addition of calcium carbonate), and an oxidant such as air
20   or oxygen is added to the solution to oxidise the arsenic
from its soluble +3 state to its insoluble +5 state.
Advantageously, because $Fe(III)$ is present in the solution
from the oxidation of pyrite in the second leaching stage,
the arsenic precipitates out as scorodite ($FeAsO_4$). As a
25   further advantage, because sulfide has been oxidised to
sulfate in the second leaching stage, the addition of
calcium carbonate can be used both to raise the solution
pH in the arsenic precipitation stage, and to precipitate
out the sulfate as calcium sulfate.
30   The arsenic and solids precipitate together with the
process solution is then passed as stream 78 to solid-
liquid separation stage 48 where the solids are filtered
from the solution. The solids residue stream 80 typically
comprises $FeAsO_4$, Fe_2O_3 and $CaSO_4$ in a form suitable for
35   disposal (e.g. as landfill). Once again, the solids may be
removed as a slurry and hence water may be needed to be
added to the process at stage 48. Thus, the preferred

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method according to the invention advantageously enables
removal of arsenic, iron and sulfur in readily disposable
forms from an original arsenopyrite concentrate.

5   Furthermore, the conditions in the arsenic
precipitation stage do not affect the precious metal
leached into solution in the leaching stage and thus the
separated solution 56 can now be passed to a precious
metal recovery stage 58, in a similar manner to the
process of Figure 1. Typically stage 58 comprises one or
10 more columns housing activated carbon onto which the
precious metals, typically gold, are adsorbed.
Periodically a gold product stream 60 is removed from
stage 58 for gold recovery (by burning or eluting the
carbon with adsorbed gold thereon).

15   As in the process of Figure 1, the solution overflow
62 from stage 58 is recycled to the leaching process, and
a proportion of the recycled stream may be drawn off to
bleed circuit 64 to separate out the contaminants which
can build up in the process, thereby producing contaminant
20 by-product stream 82.

      In further accordance with the invention, solution
recycle 62 is split to produce a first leaching stage
recycle component 84 and a second leaching stage recycle
component 86. Where the basic process solution is e.g. a
25 copper chloride solution, copper in its +2 oxidation state
is recycled to each of the leaching stages to participate
in arsenopyritic leaching in the first leaching stage and
pyrite leaching in the second leaching stage.

      Referring now to Figure 3 a process flowsheet for the
30 treatment of a double-refractory sulfidic material is
shown. In Figure 3, like reference numerals are used to
denote similar or like process stages to that of Figures 1
and 2. In addition, the upper half (ie. above the dotted
line) of the process flowsheet of Figure 3 is essentially
35 the same as that of Figure 2 and hence those process
stages will not be described again.

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In Figure 3, a double-refractory arsenopyritic
concentrate is treated. In this case, the precious metal,
typically gold, is associated with carbon and hence that
associated gold is not readily leached out of the
5   concentrate in the first or second leaching stages.
Accordingly, solids stream 76 includes solid residues
together with an associated carbon/gold component.
However, because the leaching process has substantially
removed arsenic, iron, sulfur and other contaminants to
10   acceptably low levels, the solids residue from the
leaching process is now highly suitable for roasting or
smelting in roasting stage 28.

In roasting stage 28, air and fuel together with
solids material 76 are roasted in a conventional manner,
15   producing a product stream 90 which is then fed to a gold
leaching stage 30 in a known manner. Gold leaching is
typically conducted by oxidising the roasted solids with
chlorine gas or cyanide (although chlorine gas is
preferable because it is less toxic than cyanide). In
20   further accordance with the invention, a proportion 92 of
the solution recycle stream from the arsenic precipitation
stage 42 is fed to the gold leaching stage 30.

An exhaust gas stream 94 from the roasting stage 28
(typically comprising carbon dioxide, sulfur dioxide and
25   other SO_x gases) is fed to a primary gas cleaning stage 96.
Primary gas cleaning stage typically comprises one or more
scrubbers in which water and optionally recycled wash
water are contacted with the gas stream 94.
Advantageously, any dust in gas stream 94 can be filtered.
30   Such dust may include gold chloride ($AuCl_3$) and arsenous
oxide (As_2O_3). This dust and particulates can be fed as
solids or in solution as a stream 98 back into the arsenic
precipitation stage 42 for further recovery of arsenic and
gold.
35   Residual gases from the primary gas cleaning stage 96
are passed as stream 100 to secondary gas cleaning stage
102, typically comprising gas scrubbers in which calcium

carbonate in solution is contacted with the SO_x containing gases. Product stream 104 from the secondary gas cleaning stage 102 typically therefore comprises calcium sulfate and calcium sulfite.

5   The leachate stream 106 containing dissolved gold from the gold leaching stage 30 is now passed to a solid liquid separation stage 108 to separate the gold containing solution from the solids residue. The solids residue stream 110 is passed to tails for disposal,

10   whereas the gold pregnant solution is passed to a gold recovery stage 114, typically comprising an activated carbon containing column. Carbon and adsorbed gold is periodically removed out as stream 116 for gold recovery, whereas gold depleted solution 118 is recycled to the

15   leaching/arsenic removal circuit to be combined with stream 34.

Examples

Now that optimal process flowpaths have been described, preferred examples of the method according to

20   the present invention will be described. In the following examples, an arsenopyrite concentrate from Bakyrchik, Kazakstan was processed. The aim was to develop a process that permitted processing of all samples of arsenopyrite ore provided from the Bakyrchik mine.

25

Example 1
Concentrate Characterisation.

Method:
30   6kg of concentrate was processed by ultra fine regrinding. The concentrate possessed a P_{100} 20 microns

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Product	
Laser microns	Wt% passing
20	100
18	99
15	96
12	89
10	81
8	69
6	50
5	42
3	15

The concentrate at P_{100} 20 microns was received in three cakes, the moisture content of each cake was

5   determined, and the average was used as the moisture content for the concentrate.

Cake 1
Wet sample + paper: 113.84g
10   Dry sample + paper: 85.68g
Paper: 4.83g
Dry sample: 80.85g
% Moisture: 25.8%

15   Cake 2
Wet sample + paper: 88.35g
Dry sample + paper: 66.65g
Paper: 4.83g
Dry sample: 62.02g
20   % Moisture: 25.9%

Cake 3
Wet sample + paper: 86.41g
Dry sample + paper: 68.79g
25   Paper: 4.85g

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Dry sample: 63.94g

% Moisture: 21.6%

The average moisture content determined was 24.4%. From this it was calculated that 100g of dry concentrate translated to 132.3g of the wet concentrate sample.

Example 2

Oxidation Leach

Tests were then conducted on the $P_{100} = 20$ microns reground sample to provide initial evidence of arsenic leaching via a process of oxidation. The Bakyrchik ore concentrate was noted to contain arsenic as an arsenopyrite. The reaction was designed to determine if this arsenic could be rendered soluble (and hence be selectively removed) using cupric copper as oxidant.

Method:

A 1L solution of 80g/L Cu^{2+} (as $CuCl_2$ 205.13g), 100g/L $CaCl_2$, 200g/L NaCl and 30g/L NaBr was prepared. 140g of wet concentrate (~24% moisture, therefore 105.8g dry concentrate) was added to this the solution and the resultant slurry stirred at 105°C. The pH, Eh and Fe and Cu content were measured over the course of four hours.

Solids were subsequently filtered using a Buckner apparatus and the filtrate preserved for further analysis. Solid cake was washed with low pH brine (~0.5L, 280g/L, pH 0.3), the resultant moist cake was weighed, dried in an oven and weighed again. The dry solids were preserved for further analysis.

Results and Discussion:

The pH, Eh and Fe and Cu tenor recorded over time were summarised as per the table below.

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Time (min)	pH	Eh (mV)	Fe (g/L)	Cu^{tot} (g/L)
0				
30	1.45	740	2.4	70.6
60	0.5	508	2.5	68
90	0.5	507	2.5	63
150	0.5	495	2.65	64
210	0.35	502	2.65	61
270	0.35	495	2.68	64
330	0.35	485	2.66	65

The residue assay shows an As concentration of 0.66%.
Considering a calculated mass loss of 6.5%, the As was
5   leached with an efficiency of 82.3 %

The reaction appeared to proceed quickly. A
significant drop in Eh and pH was observed within the
first hour of the reaction's progress. After this time the
10   reaction stabilised and did not appear to progress
further.

Example 3
15   Oxidation Leach
The aim of this example was to investigate whether
fresh liquor would facilitate the further leaching of the
iron/ arsenic from the previously leached material. It was
surmised that treatment of the solid obtained from the
20   previous leach would remove more of the arsenopyrite. A
fresh solution of the primary liquor was prepared and a
repeat of the previous leach was performed using the
leached material as the solid feed.

25   Method:
A 500ml solution of 80g/L Cu^{2+} (as $CuCl_2$ 102.55g),
100g/L $CaCl_2$, 200g/L NaCl and 30g/L NaBr was prepared. 30g
of the leached concentrate obtained from the previous

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oxidation was added to this solution and the resultant
slurry stirred at 105°C. pH and Eh were measured over the
course of four hours. Solids were subsequently filtered
using a Buckner apparatus and the filtrate preserved for
5 further analysis. Solid cake was washed with low pH brine
(~0.5L, 280g/L, pH 0.3), the resultant moist cake was
weighed, dried in an oven and weighed again. The dry
solids were preserved for further analysis.

   Samples taken from the solids obtained from this and
10 the previous reaction as well as the original concentrate
were digested using Aqua-regia/perchloric acid. These
solutions were then analysed for Arsenic using ICP.

Results and Discussion:
15   The pH, Eh recorded over time were summarised as per the
table below.

Time (min)	pH	Eh (mV)
0	1.32	741
0	1.2	615
30	0.55	588
60	0.31	583
90	0.29	580
120	-	579
150	0.31	569
180	0.3	574
210	0.29	574
240	0.32	572

   Wet cake + paper + filter paper: 72.5g
20 Dry cake + paper + filter paper: 40.24g
Paper + filter paper: 11.5g
Dry cake obtained: 28.74g

   The ICP analysis for Arsenic in the recovered solids
25 were summarised as per the table below:

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	As	
	Content (wt %)	Extraction (%As in concentrate)
Bakyrchik concentrate	3.49	0
Leach 1	0.66	82.3
Leach 2	0.42	88.9

As was observed in the previous leach the reaction
appeared to proceed quickly, stabilising over the course
5   of an hour. A significant drop in Eh and pH was again
observed along with a decrease in the mass of the solids
recovered when compared to the mass of the solids fed to
the solution. This suggested that there was material
left in the residue from the primary leach that was
10   still extractable. An analysis of the arsenic content of
both the feed and solid residue from both leaches
revealed a progressive reduction in the arsenic content
of the solids recovered. The results suggested that the
method could be refined to selectively leach the arsenic
15   contained within the Bakyrchik concentrates.

Example 4
Oxidation Leach
        The aim of this example was to refine the conditions
20   used in leaching arsenic from the Bakyrchik ore. Having
succeeded in leaching ~65% of the arsenic contained within
the Bakyrchik ore, the method was refined to obtain a
greater leach performance. The method focused on two
areas: firstly the leach liquor was simplified, and
25   secondly, the reaction was carried out at various

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temperatures and starting pH's to determine the effect
these changes had on improving the leach efficiency.

5 Method:

A 5L solution of 80g/L Cu^{2+} (as $CuCl_2$ 1025.64g),
150g/L $CaCl_2$ (750g) and 150g/L NaCl (750g) was prepared and
heated to 80°C. This solution was then divided into three
1.5L solutions, each solution performing an oxidation
10 leach under different conditions on the equivalent of
142.86g wet concentrate (~24% moisture, therefore 108g dry
concentrate).

Oxidation Leach Solution 1: Leach was performed at 80°C

15

Oxidation Leach Solution 2: Leach was performed at 100°C

Oxidation Leach Solution 3: Leach was performed at 80°C.
Starting pH <0.4, Eh >550mV
20

The pH and Eh of these solutions was measured over
the course of two and a half hours. Samples from each were
taken at intervals and analysed for their iron and copper
content.
25

Solids were subsequently filtered using a Buckner
apparatus and the filtrate preserved for further analysis.
Solid cake was washed with low pH brine (~1L, 280g/L, pH
0.3), and the resultant moist cake was weighed, dried in
30 an oven and weighed again. The dry solids were preserved
for further analysis.

Samples taken from the solids obtained from each
reaction as well as the original concentrate were digested
35 and analysed for arsenic, copper and iron using ICP.

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Results and Discussion:

Oxidation Leach 1 (80°C) Solution Assays

Time (min)	pH	Eh (mV)	Cu (g/L)	Fe (g/L)	As (ppm) From ICP	Comments
0	2.15	720				Solids added
0	1.58	568	71	-	-	
30	0.95	535	77	0.79	824	
60	0.75	525	77	1.14	1033	
90	0.70	520	75	1.28	1152	
120	0.70	520	75	1.41	1216	
150	0.70	516	74	1.53	1308	

5

Wet cake + paper + filter paper: 173.24g
Dry cake + paper + filter paper: 105.48g
Paper + filter paper: 11.5g
Dry cake obtained: 93.98g

10

Oxidation Leach 2 (100°C) Solution Assays

Time (min)	pH	Eh (mV)	Cu (g/L)	Fe (g/L)	As (ppm) From ICP	Comments
0	1.88	735				Solids added
0	1.5	561	71	-	-	
30	1.1	525	79	1.75	1473	
60	1.05	528	79	1.85	1532	
90	0.98	529	80	2.0	1636	
120	0.94	525	84	2.0	1678	
150	0.89	528	85	2.14	1761	

Wet cake + paper + filter paper: 170.3g
15 Dry cake + paper + filter paper: 113.32g
Paper + filter paper: 11.5g
Dry cake obtained: 101.82g

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Oxidation Leach 3 (80°C, low pH) Solution Assays

Time (min)	pH	Eh (mV)	Cu (g/L)	Fe (g/L)	As (ppm) From ICP	Comments
0	0.35	712				Solids added
0	0.8	564	71	-	-	
30	0.55	540	76	1.06	741	
60	0.43	532	74	1.41	975	
90	0.5	525	74	1.51	1082	
120	0.4	520	75	1.61	1162	
150	0.43	515	73	1.61	1181	

5   Wet cake + paper + filter paper: 172.4g

Dry cake + paper + filter paper: 108.46g

Paper + filter paper: 11.5g

Dry cake obtained: 96.96g

10   The ICP analysis for arsenic, copper and iron in the recovered solids are summarised as per the table below.

	As%	Cu%	Fe%	As% Extraction
Cons	3.22	0.09	8.38	0.0
Leach 1	1.07	0.31	5.22	71.1
Leach 2	0.25	0.30	2.85	92.7
Leach 3	1.57	0.30	5.40	56.2

These results clearly indicate that the rate of reaction
15   is significantly higher at 100°C than at 80°C.

Example 5

Iron/Arsenic Rejection process

20   Method:

        Liquor obtained from a previous oxidation reaction (10L) was returned to the vat and heated to 80°C with low

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stirring. Upon reaching this temperature the pH and Eh of
the liquor were measured and a sample taken. The liquor
was then aerated (100L/hr) with agitation, and the pH and
Eh of the liquor was measured and a sample was taken every
5   thirty minutes thereafter. After four hours the rejection
process was considered to be complete, the liquor was
filtered using a Bucher apparatus and the rejected
precipitate was removed as a filter cake. The wet cake was
weighed, and then dried over twenty-four hours in an oven.
10   The dry cake was then weighed and a sample digested for
analysis.

Results and Discussion:

The pH and Eh and tenor of the liquor over time were
summarised as per the table below.

15

Time mins	pH	Eh (mV)	Sample No.	As (g/L)	Fe (g/L)	AAS Cu (g/L)	AAS Fe (g/L)	Comments
0	0.7	500	1	2.8	3.7	88	3.7	Vol:10L
0	0.7	500	-	-	-	-	-	air@100L/Hr
30	1.1	510	2	2.3	3.6	90	3.3	
60	1.5	520	3	1.2	2.7	90	2.6	
90	1.6	525	4	0.6	2.4	91	2.2	
120	2.0	530	5	0.3	1.3	85	1.6	
150	2.1	535	-	-	-	-	-	
180	2.1	545	-	-	-	-	-	
210	2.2	555	-	-	-	-	-	
240	2.5	570	6	ND	0.5	88	<0.1	Cu^{tot} 88, Cu^{2+}:88

Wet cake + paper + filter paper: 257.2g

Dry cake + paper + filter paper: 128.94g

Paper + filter paper: 11.5g

Dry cake obtained: 117.44g

20

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Analysis of the precipitate shows the following results:

Element	Concentration (wt. %)
As	19.0%
Fe	33.8%
Cu	1.5%

5　Over the four hour period of the experiment, essentially 100% of both the iron and arsenic were precipitated, whilst concurrently the oxidation potential (Eh) was restored to a level higher enough to be used for further leaching. The Fe/As molecular ration being 2.4, it is

10　anticipated that FeAsS was precipitated with other Fe based compounds.

Example 6

15　**Iron/Arsenic Rejection process**
Method:

　　Liquor obtained from the oxidation reaction (10L) was returned to the vat and heated to 80°C with low stirring. Upon reaching this temperature the pH and Eh of the liquor

20　were measured and a sample taken. The liquor was then aerated (100L/Hr) with agitation, and the pH and Eh of the liquor was measured and a sample was taken every thirty minutes thereafter. After four hours the rejection process was considered to be complete, the liquor was filtered

25　using a Bucher apparatus and the rejected iron precipitate was removed as a filter cake. The wet cake was weighed, and then dried over twenty-four hours in an oven. The dry cake was then weighed and a sample digested for analysis.
Results and Discussion:

30　　　The pH and Eh and tenor of the liquor over time were summarised as per the table below.

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Time mins	pH	Eh (mV)	Sample No.	As (g/L)	Fe (g/L)	AAS Cu(g/L)	AAS Fe (g/L)	Comments
0	0.7	500	1	2.8	3.7	88	3.7	Vol:10L
0	0.7	500	-	-	-	-	-	air@100L/Hr
30	1.1	510	2	2.3	3.6	90	3.3	
60	1.5	520	3	1.2	2.7	90	2.6	
90	1.6	525	4	0.6	2.4	91	2.2	
120	2.0	530	5	0.3	1.3	85	1.6	
150	2.1	535	-	-	-	-	-	
180	2.1	545	-	-	-	-	-	
210	2.2	555	-	-	-	-	-	
240	2.5	570	6	ND	0.5	88	<0.1	Cu^{tot} 88, Cu^{2+}:88

Wet cake + paper + filter paper: 257.2g

Dry cake + paper + filter paper: 128.94g

Paper + filter paper: 11.5g

Dry cake obtained: 117.44g

5   Moisture component: 128.26g (47.8%)

Example 7

Leach on regenerated liquor, lower slurry density

Method:

10   A 90g sample of wet concentrate (~24% moisture, therefore 68g dry concentrate) was added to the liquor obtained from the oxidation reaction (1.5L) and the resultant slurry stirred at 100-105°C. The pH and Eh of the liquor were monitored and a sample taken every thirty

15   minutes over a four hour period. After this period the liquor was filtered using a Bucher apparatus and the filter cake removed, the wet cake was weighed and then dried over twenty-four hours in an oven. The dry cake was then weighed and a sample digested for analysis.

20   Results and Discussion:

The pH and Eh and tenor of the liquor over time is summarised in the table below.

Time (min)	pH	Eh (mV)	Sample No.	AAS Cu (g/L)	AAS Fe (g/L)	ICP As (g/L)	ICP Cu (g/L)	ICP Fe (g/L)
0	2.5	600	-	-	-			
10	1.8	555	-	-	-			
30	1.5	550	1	90	1.5			
60	1.3	545	2	89	1.1			
90	1.2	540	3	87	1.2			
120	1.1	540	4	67	0.8			
150	1.1	535	5	88	1.0			
180	1.0	535	6	85	1.0			
210	1.0	535	7	88	1.0			
240	1.0	536	8	87	1.1			

Dry cake obtained: 58g

5   First & Second Leaching Stage Examples

Example 8

First Stage Leaching

In this example, the aim was to confirm through a
simulation of a continuous process that the operating
10   conditions used for batch testing would apply to a
commercial operation. This experiment also provided
material to be used for a pyrite oxidation at atmospheric
pressure.

As shown in Figure 5, continuous operation under
15   conditions similar to the batch processes of Examples 2 to
4 consistently delivered an As extraction of 85%.

Procedure

7.5 litre titanium reactors were employed, with the
overflow from the first connected to the second, which
20   subsequently overflowed into a holding tank. During
continuous operation, 2 litres/hr of solution was fed to
the first reactor from a feed tank using a peristaltic
pump. The solids addition rate was 144g/h and was achieved

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through 24g (dry basis) batch additions of concentrate to the first reactor every 10 minutes.

Initially a 30 litre stock solution containing 80g/l Cu^{2+}, 200g/l NaCl, 100g/l $CaCl_2$, and pH<1 was prepared. To

5   each reactor, 7.5 1 of stock solution was added and maintained at 100°C, with 360g of dry equivalent P80 - 30 microns low grade gold (30 gr/tonne) concentrate added and the resultant slurry agitated and monitored every 30 mins for Eh, pH, As, Fe and Cu. After 3 hours, a 100ml slurry

10   sample was taken and filtered in a Buchner funnel and washed with acidic brine solution. The solids were then dried and assayed by ICP for copper, arsenic and iron.

After 3 hours, continuous operation was conducted (as described) for a further 10 hours, with a 200ml slurry

15   sample taken every 2 hours and filtered as described above. The solids were then dried and assayed by ICP for copper, arsenic and iron.

The results are summarised in the following tables:

Tank 1

Ref #	Solid Sample	Time (min)	Sample (#)	T (°C)	Eh mV	pH	Cu (gpl)	Fe (gpl)	As (gpl)	Comments
0		0	0	95	620	1	77	0	0	
1										Added 720g dry solids
2		60	1	100	520	0.5	87	2.6	2.3	All additions below are in "as is" moist concentrate
3		120	2	100	520	0.5	83	2.7	2.3	192.95 g added over the hour
4		180	3	90	530	0.7	81	1.7	1.4	187.9 g added over the hour
5		240	4	98	535	0.6	88	1.9	1.6	183.4 g added over the hour
6		300	5	103	540	0.4	89	2.5	2.1	189.65 g added over the hour
7	1	360	6	109	530	0.2	74	2.2	1.9	195.44 g added over the hour
8		420	7	109	535	0.2	95	3.7	3.3	194.42g added over the hour
9	2	480	unstable	conditions						81.61g added over the hour
10		540	8	106	525	0.2	95	4.9	4.5	200g added over the hour
11		600	9	102	524	0.3	95	4.2	3.8	198.79 added over the hour
12	3	660	10	70	509	0.7	98	3.2	2.6	62.82g added over the hour
13	4	680	11	74	501	0.8	99	3	2.4	

Tank 2

Ref #	Hours	Time (min)	Sample (#)	T (°C)	Eh mV	pH	Cu (gpl)	Fe (gpl)	As (gpl)
0		0	0	80	620				
1									
2		60	1	85	530	0.9	77	1.3	1
3		120	2	86	530	0.8	81	1.5	1.2
4		180	3	90	530	0.7	84	1.7	1.5
5		240	4	88	530	0.6	86	1.8	1.6
6		300	5	85	525	0.5	91	2.1	1.8
7		360	6	85	520	0.4	95	2.2	2
8		420	7	85	520	0.4	105	2.7	2.3
9		480	unstable	conditions					
10		540	8	84	519	0.4	99	2.8	2.5
11		600	9	83	514	0.4	98	3.2	2.9
12		660	10	83	516	0.4	98	3.5	3.1
13		680	11	85	512	0.4	99	3.3	2.94

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Solid Analysis Feed and Tank 2
overflow

Ref #	Description	Fe (%)	As (%)	Cu (%)	As Extraction (%)	Mass Loss (%)
	Feed	8.60	3.20	0.08	0.00	0.00
1	Tank 2 - Solids 1	4.25	0.58	0.50	83.1	6.55
2	- Solids 2	4.15	0.42	0.52	87.8	6.79
3	- Solids 3	4.55	0.51	0.55	85.1	6.27
4	- Solids 4	4.15	0.51	0.42	85.1	6.80
mix	- Solids 5	4.50	0.52	0.42	84.8	6.44
	Average				85.2	6.57

5   Example 9

Second Stage Leaching

The aim of this experiment was to evaluate the
possibility of oxidising the pyrite component of the
residue from an As leach, at atmospheric pressure with
10   pure oxygen. 500 g of the residue obtained during the
continuous leach test of Example 8 was used in this
experiment.

The pyrite was successfully oxidised with oxygen at

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atmospheric pressure and 105 °C. The final As and Fe extraction were both above 95 %. The $S_{(e)}$ (elemental sulfur) in the oxidation residue was equivalent to the sulfur associated with the arsenopyrite in the
5　concentrate. The results are presented graphically in Figure 6.

Procedure

　　A 7.5 L titanium reactor was prepared with a turbine agitator for gas dispersion and the appropriate titanium
10　gas injector on a large yellow hotplate. 5 L of brine solution was prepared in 7.5 L titanium reactor with the following composition:

250 g/L NaCl, 50 g/L $CaCl_2$, 20 g/L Cu (from cupric chloride) and pH adjusted < 1.0.

15　　　A representative sample of dry As leach residue from Example 8 was sent to an external lab to analyse for elemental S, total S, Au, Fe and As.

　　With the agitator drive set at 80 Hz on the VSD, the temperature of the solution was raised to 105°C, sample
20　t=0 is taken, Eh & pH were monitored and 500g of dry arsenic leach residue from Example 8 was introduced into the solution. After 30 minutes, a sample of solution was taken for Fe, As & Cu analysis and Eh and pH were monitored.

25　　　Oxygen was introduced at the rate of 1 L/min. Eh, pH, Fe, Cu and As were monitored every 30 minutes for the first 3 hours and every hour after that. When the soluble Fe assay stopped increasing, the experiment was considered complete.

30　　　The last sample was taken, the suspension filtered, the cake washed twice with acidic brine followed by hot water until the filtrate was clear. The washed cake was

- 40 -

dried, weighed and analysed for As, Fe, Cu, C, elemental S and total S.

Experimental Results

The following experimental results were observed

5 Final Leach Solid Weight

Cake:

Wet cake + paper + filter paper: 744.27

Dry cake + paper + filter paper: 490.96

Paper + filter paper: 66.09

10 Dry cake obtained: 424.87

Mass reduction: 15 %

Solid Analysis feed to Pyrite Oxidation with Oxygen

Information in dry wt % or ppm as noted

Description	Fe (%)	As (%)	Cu (%)	Au ppm	S_t (%)	S_e (%)
Total	4.31	0.55	0.61	-	-	-
Soluble	0.01	0.03	0.10	-	-	-
Insoluble	4.30	0.51	0.51			

15 Solid Analysis residue from Pyrite Oxidation with Oxygen

Information in dry wt % or ppm as noted

Description	Fe (%)	As (%)	Cu (%)	Au ppm	S_t (%)	S_e (%)
Total	0.52	0.19	0.35	-	-	-
Soluble	0.01	0.01	0.01	-	-	-
Insoluble	0.51	0.18	0.34	-	-	-

Fe & As Extraction from Concentrate to Pyrite Oxidation

20 residue

Both As and Fe extraction exceeded 95% as demonstrated in the following tables:

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Ref #	Mins	Sample (#)	T (°C)	O₂ (l/min)	Eh mV	pH	Cu (gpl) AA	Fe (gpl) AA	Fe (gpl) ICP	As (gpl) ICP	Cu (gpl) ICP	Comments
0	0	1	82	0.5	645	0.82	-	0	0	0	20	Added conc
1	30	2	91	0.5	570	0.82	-	0.15	0.21	0.08	18	
2	60	3	90	0.5	572	082	-	0.22	0.29	0.10	18	Frothing too much
3	90	-	88	0.5	580	0.91	-					
4	120	-	87	0.5	577	0.92	-					
5	150	-	83	0.5	580	1.01	-					
6	180	4	88	0.5	570	0.95	-	0.39			18	
7	210	-	91	0.5	580	0.95						
8												Stopped and transferred into la... Added 5 litre of fresh solut
9												Vol= 13 litres

Ref #	Mins	Sample (#)	T (°C)	O₂ (l/min)	Eh mV	pH	Cu (gpl) AA	Fe (gpl) AA	Fe (gpl) ICP	As (gpl) ICP	Cu (gpl) ICP	Comments
1	0	1	101	1	530	0.9	18.5	0.5	0.6	0.13	18.1	
2	30		104	1	582	1						
3	60		105	1	585	0.95						
4	90		105	1	585	0.97						
5	120		105	1	583	1.07						
6	150		105	1	582	1.14						
7	180	2	108	1	593	1	18.8	0.9	1.0	0.19	18.6	
8	210		103	1	599	1						
9	240		105	1	600	0.95						
10	270		105	1	585	0.93						
11	300		103	1	600	0.93						New pH probe. The old one app faulty as there was hardly any
12	360	3	102	1	610	<0.1	19.8	1.2	1.5	0.25	21.2	
13	390		102	1	609	<0.1						
14	420	4	105	1	606	<0.1	21	1.3	1.6	0.27	21.6	
15	450		105	1	616	<0.1						
16	480	5	105	1	614	<0.1	20.9	1.4	1.5	0.26	19.9	
17	480		105	1	605	<0.1						
18	540		105	1	625	<0.1						
19	570		105	1	630	<0.1						
20	600	6	105	1	627	<0.1	26.2	1.8	1.7	0.33	24.4	
21	630		105	1	630	<0.1						
22	660	7	105	1	629	<0.1	27.1	1.8	1.9	0.34	25.1	
23	690		105	1	622	<0.1						
24	720		105	1	624	<0.1						
25	750	8	105	1	625	<0.1	25.2	1.8	1.7	0.31	23.2	
26	810											
27												

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Pyrite oxidation, feed vs. residue:

	Wt %		Mass (g)	
	Feed	Residue	Feed	Residue
			500	424.9
Fe	4.3	0.51	21.6	2.2
As	0.5	0.18	2.6	0.8

Equivalent Concentrate

5

	Mass (g)	Concentration (%)
	535.2	100
As	17.1g	3.2
FeAsS	37.2	7.0
Fe	46.0	8.6
FeS_2	25.6	4.8
S	29.4	5.5
S in FeAsS	7.3	1.4
S in FeS_2	22.1	4.1
Fe in AsFeS	12.8	2.4
Fe in FeS2	19.3	3.6
Fe other	14.0	2.6

Fe and As extraction from Concentrate to Pyrite Oxidation residue:

Fe   95.3%
As   95.5%

10

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Extraction of elemental sulphur from the pyrite oxidation residue demonstrated the $S_{(e)}$ is equivalent to the S associated with the AsFeS or 1.4 % in the concentrate

5

Elemental Sulfur Extraction		
Float Head Sample weight	8.68 g	100%
$S_{(e)}$ extraction residue		
Total	0.35 g	
Carbon	0.21 g	
$S_{(e)}$	0.14 g	1.6%
Mass Change		79%
$S_{(e)}$ related to concentrate		1.28%

Now that preferred operating details of the process have been exemplified, it will be appreciated by those skilled in the art that the method of the present

10   invention includes the following advantages:

- The method can be employed to recover precious metals from sulfidic ores and concentrates which are otherwise difficult or impossible to treat using conventional available processes/techniques such as smelting and

15   roasting.

- The method can accommodate a high carbon content in such ores, because the method is conducted in solution, and thus blinding agents can be employed to prevent precious metal adsorption onto carbon, which can otherwise

20   interfere with precious metal recovery.

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- The method can be employed to remove contaminants from a wide variety of ore and concentrate feedstocks which, once removed, can then be treated using conventional smelting/roasting techniques.

5 - In this regard, the method enables removal of arsenic, iron and sulfur in readily disposable forms from an original arsenopyrite concentrate, leaving a readily treatable concentrate.

- The method has the capacity to recover a wide variety of
10 metals of economic value, especially precious metals, using simple non-cyanide based leaching and separation processes, and including activated carbon adsorption.

- The method can be used to treat contaminated residues to allow them to be subsequently disposed of with reduced
15 environmental impact.

Whilst the invention has been described with reference to a number of preferred embodiments, it should be appreciated that the invention can be embodied in many other forms.

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CLAIMS

1.   A method of removing a contaminant from a sulfidic material comprising the steps of:
• mixing the material in an aqueous solution wherein a multi-valent species of a relatively high oxidation state oxidises the contaminant to render it soluble in the solution, produces a contaminant refined material, and is reduced to a relatively lower oxidation state; and
• removing the contaminant from the solution whilst regenerating the multi-valent species to its relatively high oxidation state.

2.   A method of removing a contaminant from a sulfidic material comprising the steps of:
• mixing the material in an aqueous solution having an oxidation potential controlled to oxidise substantially only the contaminant to render it soluble in the solution, thereby producing a contaminant refined material; and
• separating the solution from the contaminant refined material.

3. A method as claimed in claim 1 or 2 wherein the contaminant is removed from the solution by precipitation through the introduction of an oxidant into the solution in a precipitation stage.

4. A method as claimed in claim 3 when dependant on claim 1 wherein the oxidant simultaneously causes the multi-valent species to be oxidised to its relatively high oxidation state.

5.   A method as claimed in claim 4 wherein, after precipitating and removing the contaminant and regenerating the multi-valent species to its higher oxidation state, the solution is recycled to the mixing stage.

6.   A method as claimed in any one of claims 3 to 5 wherein in the precipitation stage the solution pH is maintained at around pH 2-3.

7. A method as claimed in claim 6 wherein the solution pH is maintained by regulating the supply to the solution of the oxidant and/or an alkali agent.

8. A method as claimed in any one of the preceding claims wherein the contaminant is oxidised in a single or multi stage leaching process.

9. A method as claimed in claim 8 wherein the leaching process comprises a first leaching stage in which the oxidation potential is controlled to oxidise substantially only the contaminant to render it soluble in the solution, and a second leaching stage in which the oxidation potential is increased to oxidise sulfide in the contaminant refined material.

10. A method as claimed in claim 9 wherein the sulfidic material is a pyritic material, and in the first leaching the stage the contaminant is oxidised at a solution Eh sufficient to oxidise the contaminant and leach it into solution but not substantially leach pyrite.

11. A method as claimed in claim 10 wherein in the first leaching the stage the solution pH is less than 1, the solution Eh is around 0.5 volts, and the solution temperature is around 105°C.

12. A method as claimed in any one of claims 9 to 11 wherein the sulfidic material is a pyritic material, and in the second leaching stage the pyritic material is oxidised at a higher solution Eh then the first leaching stage, the Eh being sufficient to leach pyrite.

13. A method as claimed in claim 12 wherein the solution pH is less than 1, the solution Eh is around 0.6 volts, and the solution temperature is about 105°C.

14. A method as claimed in claim 12 or 13 wherein to achieve the higher solution Eh in the second leaching stage an oxidant such as oxygen, air, chlorine gas, or hydrogen peroxide is added to the solution.

15. A method as claimed in any one of claims 12 to 14 wherein in the second leaching stage a low pH in the

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solution is maintained by adding thereto an acid such as sulphuric acid or hydrochloric acid.

16. A method as claimed in any one of claims 9 to 15 wherein solution is separated from the material after each

5　leaching stage for removal of contaminant therefrom.

17. A method as claimed in claim 16 wherein the separated solution from each leaching stage is combined, and contaminant is removed from the combined solution by precipitation in a manner as defined in any one of claims

10　3 to 7.

18. A method as claimed in claim 16 or 17 wherein contaminant refined material that is separated from the solution after the first leaching stage is fed to the second leaching stage.

15　19. A method as claimed in any one of the preceding claims wherein the aqueous solution includes a dissolved metal chloride.

20. A method as claimed in claim 19 wherein the chloride concentration is approximately 7 moles/litre.

20　21. A method as claimed in claim 19 or 20 wherein the metal in the dissolved metal chloride functions as the multi-valent species.

22. A method as claimed in claim 21 wherein the metal in the metal chloride is copper or iron.

25　23. A method as claimed in claim 22 wherein in the higher oxidation state the metal is $Cu(II)$ or $Fe(III)$ and in the lower oxidation state the metal is $Cu(I)$ or $Fe(II)$.

24. A method as claimed in any one of the preceding claims wherein the sulfidic material is a pyritic ore or

30　concentrate.

25. A method as claimed in any one of the preceding claims wherein the contaminant is arsenic, antimony or bismuth present in the sulfidic material.

26. A method as claimed in any one of the preceding claims

35　wherein after removing the contaminant the solution is recycled to the leaching stage.

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27. A method as claimed in any one of the preceding claims
wherein the sulfidic material comprises, in addition to
the contaminant, a metal to be recovered, the method
further comprising a metal recovery stage to recover metal
5   from the separated contaminant refined material.

28. A method as claimed in claim 27 wherein a separate
metal recovery stage is provided after contaminant
oxidation, and additionally or alternatively is provided
in-line prior and/or subsequent to contaminant
10 precipitation.

29. A method as claimed in claim 27 or 28 wherein the
sulfidic material is a double-refractory ore, and the
metal recovery stage is provided as a separate, subsequent
stage, to recover metal present in contaminant refined
15 material solids from the leaching process.

30. A method as claimed in claim 29 wherein the metal
recovery stage comprises a conventional roasting or
smelting process to which the contaminant refined material
solids from the leaching process is fed.

20 31. A method as claimed in claim 30 wherein chlorine or
cyanide leaching is employed after roasting to recover any
remaining metal in the roasted solids material.

32. A method as claimed in claim 27 or 28 wherein the
sulfidic material is a single refractory ore and the metal
25 recovery stage is provided in-line and subsequent to
contaminant precipitation.

33. A method as claimed in claim 32 wherein metal recovery
involves adsorption of the metal in solution onto carbon
in a column containing activated carbon.

30 34. A method as claimed in any one of claims 27 to 33
wherein the metal is a precious metal such as gold,
silver, platinum or other platinum group metal.

35. A method as claimed in any one of claims 27 to 34
wherein after a first leaching stage the solution is
35 subjected to a thickening stage to thicken and separate
contaminant refined material from the solution.

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36. A method as claimed in any one of claims 27 to 35 wherein after a second leaching stage the contaminant refined material is filtered from the solution for metal recovery or disposal.

5   37. A method as claimed in any one of claims 27 to 36 wherein the contaminant is filtered from the solution after contaminant precipitation and prior to in-line metal recovery.

38.   A method of removing arsenic from a gold-bearing

10   pyritic material comprising the steps of:

•leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride solution in which the metal has a relatively high oxidation state, such that the metal oxidises the arsenic

15   to render it soluble in the solution, produces a pyritic material refined of arsenic, and is reduced to a relatively lower oxidation state;

•precipitating and separating the arsenic from the solution in a precipitation stage whilst simultaneously

20   regenerating the metal to its relatively high oxidation state; and

•returning the solution to the leaching stage with metal in its relatively high oxidation state.

39. A method as claimed in claim 38 which is otherwise as

25   defined in any one of claims 2 to 37.

40. A method of removing arsenic from a gold-bearing pyritic material comprising the steps of:

•leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride

30   solution having an oxidation potential controlled to oxidise substantially only the arsenic to render it soluble in the solution, thereby producing a pyritic material refined of arsenic; and

separating the solution from the refined pyritic material.

35   41. A method as claimed in claim 40 which is otherwise as defined in any one of claims 1 or 3 to 37.

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42. A method of treating a relatively high carbon content sulfidic material contaminated with a contaminant to allow recovery of a precious metal present with the material, comprising the steps of:

5   •leaching the material in an aqueous solution wherein the contaminant and metal are solubilised in the solution, whilst masking the carbon in the material to prevent precious metal adsorption thereon; and
recovering the precious metal from the solution.

10 43. Any metal produced by the method of any one of the preceding claims.

Dated this 2nd day of May 2003

15

By its Patent Attorneys
GRIFFITH HACK
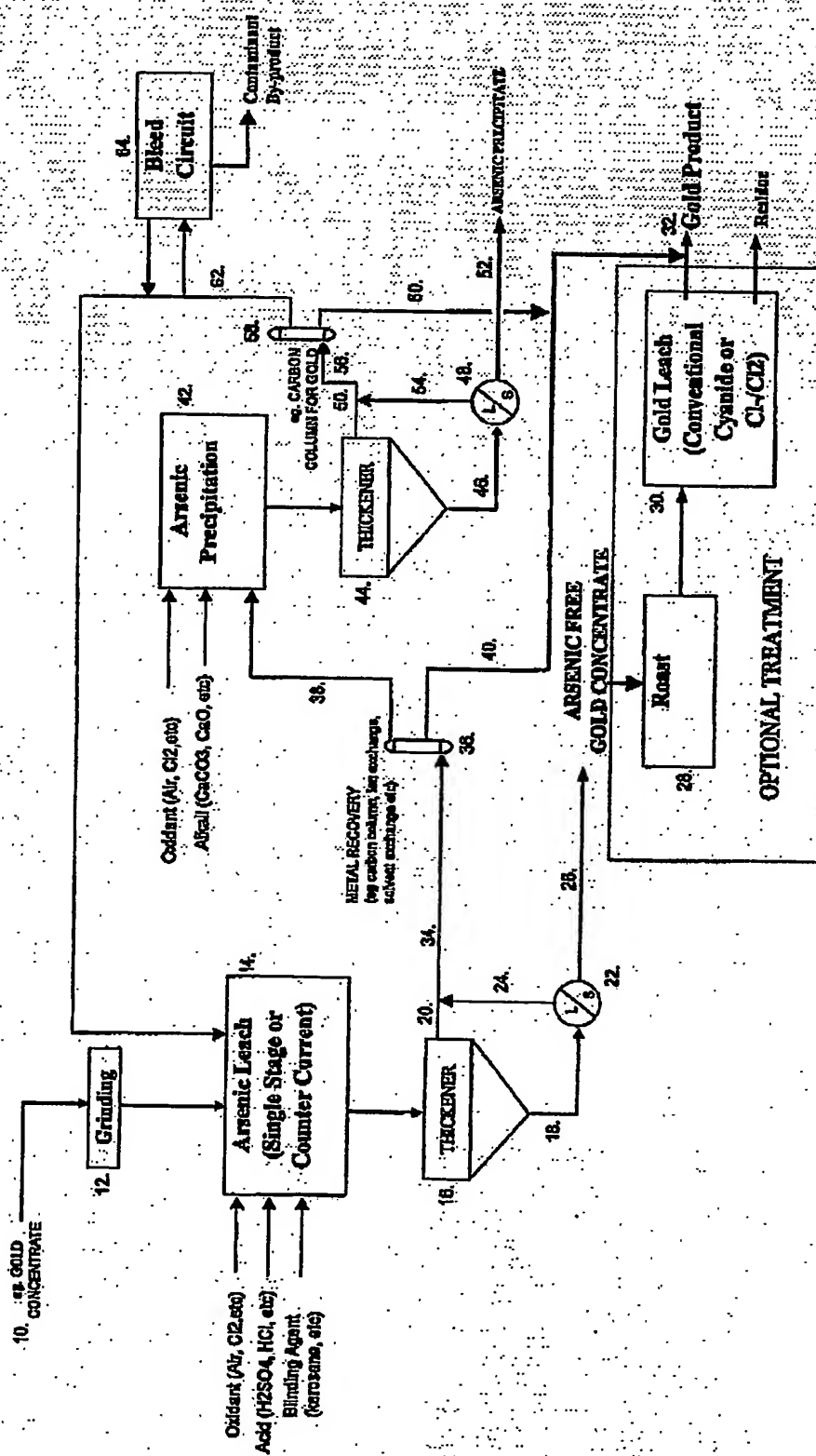
FIGURE 1

FIGURE 2

Flowsheet for Single-Refractory Gold Concentrates
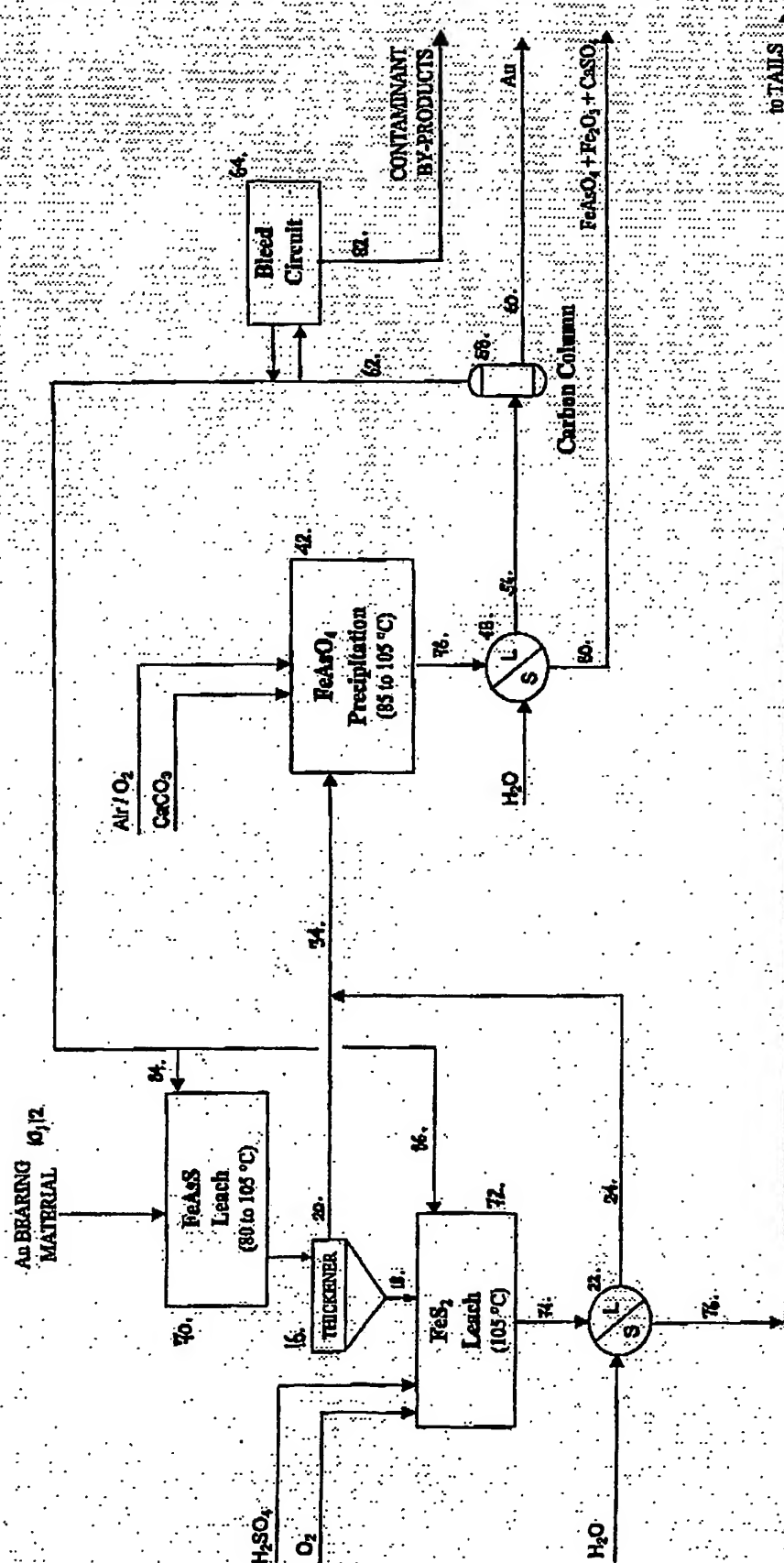
FIGURE 3

Flowsheet for Double-Refractory Gold Concentrates
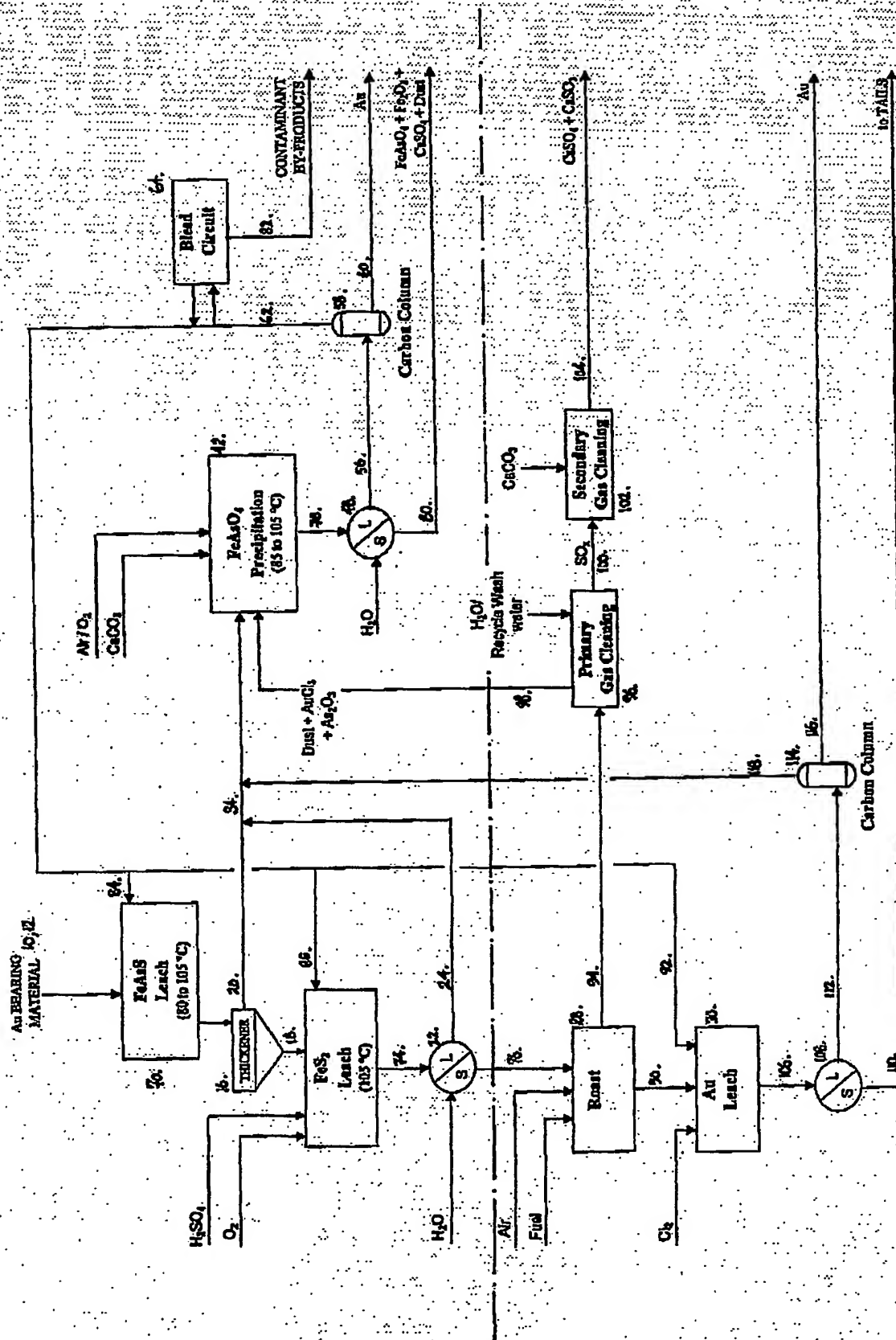
FIGURE 4
Continuous As Leach
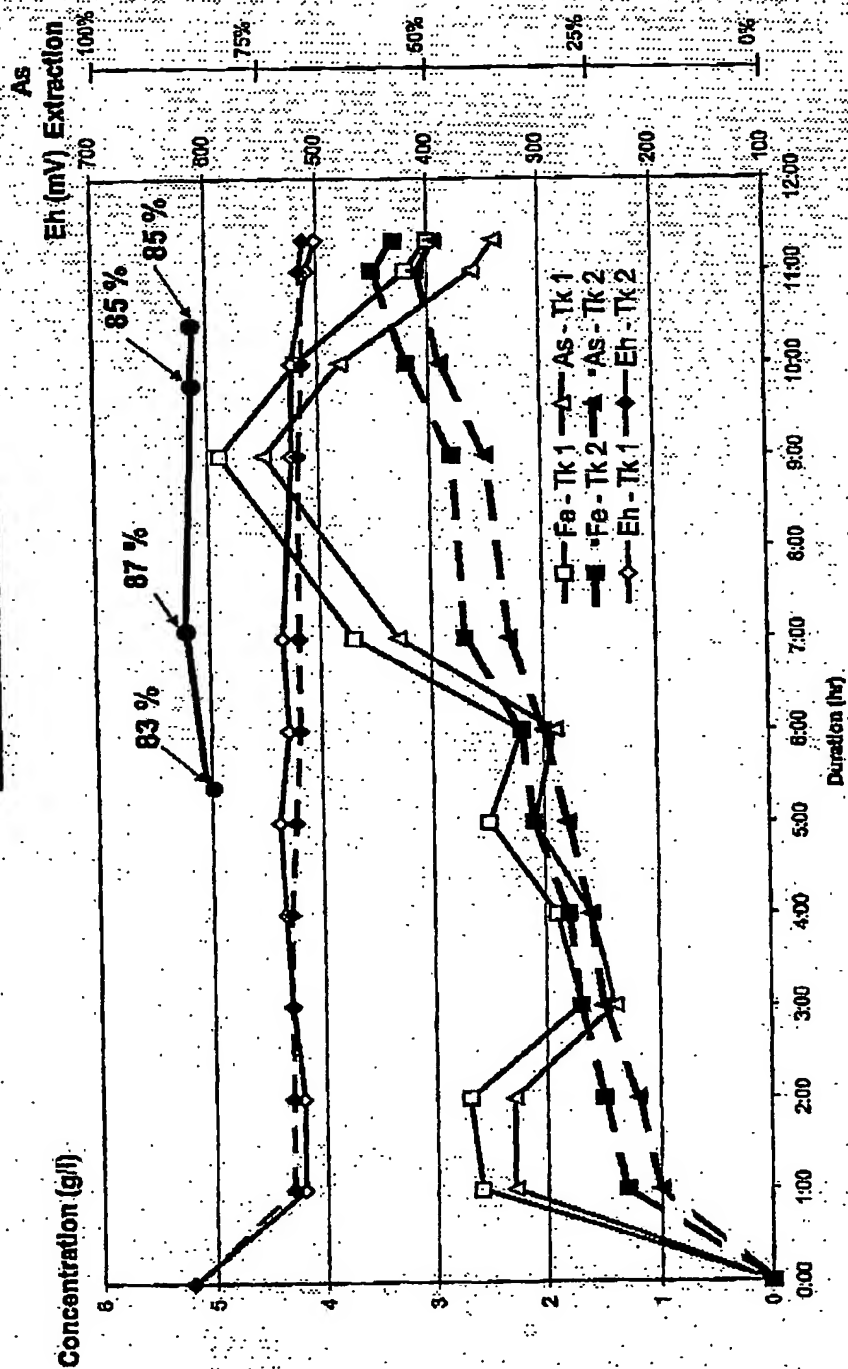
FIGURE 5

Pyrite Oxidation